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LAND TREATMENT FIELD STUDIES

Volume 6. Inorganic Pickling Liquor Waste

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16. ABSTRACT

This report presents the results of field measurements and observations of a land treatment site for the management of an inorganic pickling liquor waste. The waste is spread on the site as a 20% solids sludge. Sulfate and iron are known to be major waste constituents. The organic content of the waste is neglible. The site was sampled twice, and observations were made on the type and amount of waste handled, site characteristics, and management procedures for waste application and monitoring. Organic and inorganic analysis was conducted on the waste and soil/waste mixture; inorganic analysis was performed on plant samples.

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

This report provides the results of a field study investigation of one of six sites receiving industrial waste sludges by land cultivation. The purpose of the study was to identify and verify parameters which lead to environmental acceptability of the waste, and to recommend research needs for establishing guidelines and criteria for land cultivation.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

ABSTRACT

This report presents the results of field measurements and observations of a land treatment site for the management of an inorganic pickling liquor waste. The waste is spread on the site as a 20% solids sludge. Sulfate and iron are known to be major waste constituents. The organic content of the waste is neglible. The site was sampled twice, and observations were made on the type and amount of waste handled, site characteristics, and management procedures for waste application and monitoring. Organic and inorganic analysis was conducted on the waste and soil/waste mixture; inorganic analysis was performed on plant samples.

The site is a portion of a 300-acre farm which is leased by the waste generator. Prior to leasing the site, the owner indicated that the land had been used for farming and he intends to return the land to farm use in the future. Management of the land treatment site is informal. Monitoring of the soil/waste mixture for pH amendment requirements is done three times a year by the state government.

No farming activity is presently being conducted on the site. Corn, hay, and oats are grown on land in the vicinity of the site. Surface run-off appears to be a problem at the site. Although the run-off does not threaten any surface waters in the vicinity, it does pose a possible contamination problem to adjacent farmland. Also, the waste/soil mixture at the site is acidic and could promote the migration of acid soluble metals. It is not clear if the potential migration would have a significant environmental impact.

The land treatment operation could be improved by eliminating the surface run-off conditions and more frequent monitoring and adjustment of the waste/soil pH. Better record keeping practices should also be instituted and utilized for planning continued activities at the site and developing a post closure plan.

This report was submitted in fulfillment of Contract No. 68-03-2602 by Arthur D. Little, Inc., under sponsorship of the U.S. Environmental Protection Agency. This report covers the period September 1977 through February 1981 and work was completed as of May 1981.

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SECTION 1

INTRODUCTION

Land treatment is the application and incorporation of solid or semisolid waste into surficial soils. Other terms used to describe this practice include land farming, land cultivation, refuse farming, land spreading, soil farming and soil incorporation. The term land application, on the other hand, usually refers to irrigation of surficial soil with wastewater. Land treatment is essentially a physical/chemical/biological waste treatment method that utilizes the natural capacity of the soil system to aerobically degrade, assimilate and immobilize certain waste constituents.

At every land treatment site, there is a dynamic balance of decomposition, attenuation and migration of waste constituents. The extent to which any one of these mechanisms occurs depends on the waste character, site character and cultivation procedures.

A land treatment site should provide decomposition of the organic constituents applied and incorporated. The migration of soluble constituents from a land treatment site should be within environmentally acceptable concentrations for the receiving media, particularly ground and surface waters. The attenuation of remaining constituents over the design life of the site should not lead to a build up total concentrations that could harm the soil structure, cause phytotoxicity, or lead to excessive concentrations in the food web through bioaccumulation.

From the above discussions, it is evident that site-specific characteristics and waste characteristics together are key to achieving environmentally optimal use of surficial soils in waste treatment. Equally important (although not as evident) is the management of the land cultivation operation; no matter how optimal conditions may be for degradation/attenuation of waste, some sites can be overloaded. Management of a site can be viewed as the means through which desired waste treatment conditions are maintained.

OBJECTIVES

The objective of this study was to determine the environmental acceptability of land treatment of a neutralized acid pickle sludge. Currently the site is utilized only for land treatment of waste. In this study we address the issues of environmental impact of the land treatment on surrounding areas and potential impacts on future uses of the site.

DESCRIPTION OF THE SITE

This site is a portion of a 300 acre farm which is dedicated to the land treatment of an inorganic pickling liquor waste. The site is leased to the waste generator. Another portion of the farm is leased by the owner to a nearby city which operates a sanitary landfill on the property.

This site and its immediate vicinity are rural farmland. Corn, hay, and oats are the major crops in this region. Aside from the owner's farmhouse, which is located less than 100 feet from the land treatment site, the nearest houses appear to be at least a mile away. The site was previously used as farmland, and the farmer indicated that he intends to put the land back into condition suitable for cultivation after completion of land treatment operations.

Waste Characteristics

Wastes applied to this land treatment site consist of neutralized pickling liquor from a facility producing fabricated metal products (SIC Code 349). The waste is spread on the site as a 20% solids sludge (80% water). Iron is known to be a major constituent of this waste. Sulfate accounts for 35% of the dried solids. Other constituents found in significant concentrations in the wastes are calcium, phosphorus, potassium, and magnesium. Chromium, copper, lead, and zinc were present at the part per million level. The organic content of the wastes is negligible.

Spent sulfuric acid from the pickling operation (2-4% acid) is stored in a brick-lined tank at the waste generation site. The tank has sufficient storage for about three batches of spent acid, and the normal holding time in this tank is one week or less. Prior to transport to the land treatment site, the spent acid is neutralized with a dilute lime slurry to a target pH of 9-10. Lime slurry additions are made directly to a tank truck which is equipped with an electrically propelled mixer blade. Approximately 600,000 gallons of neutralized spent pickling liquor are land treated each year.

Site Characteristics

While the environs of this site represent variable topography, the site itself is located on a levelled hilltop. The hilltop slopes to the north into a holding pond used for storage of wastes when conditions are not suitable for immediate application. The site is not fenced, but berms have been constructed to the north behind a waste storage lagoon, to the west and to the south. The downslope of the hill has been terraced to the west. A stand of trees visually separates the land treatment site from the farmhouse. Otherwise, the only existing buffers are those that were constructed for erosion protection. The site itself is accessible via a dirt road connecting the driveway of the farm to the site itself. During wet weather, heavy vehicles cannot get on the application areas of the site.

Soil conditions in this region are typified by two general soil associations. Topsoils have been classified as silty loam and silty clay loams which

are slightly to moderately acidic. The surface soils range from 10 to 20 inches thick and occur over coarse silt loams (which may be up to 40 inches thick), silt loesses (with thicknesses that range from less than 2 feet to 8 feet), or in some places, clay loam tills. The subsoils are then underlain by bedrock. Thus, the distance to bedrock can be as little as 5 feet or less in some areas. Generally the soils are well drained and fertile.

Groundwater is located 200 feet below the residence on the farm. Average well depths in the area exceed 450 feet. A surface stream is located 1/2 to 1-1/2 miles to the north of the site.

Topographical conditions, soil conditions, ground and surface water characteristics, and regional meteorological conditions are summarized in Table 1.

The ecological diversity at the site appears limited to plant life such as alfalfa which is associated with farming activities in the surrounding area. Rodents and terrestrial birds are likely users of the site because of its proximity to a sanitary landfill. The surrounding area is typified by agriculture land and early-successional decidious woodlands which support a diverse plant and animal population.

Transfer of Waste to the Site

The farm is located approximately five and one-half miles from the waste generation site. Wastes are transported by a contract hauler. The transport tank has a nominal capacity of 1,500-1,600 gallons and was custom made by the waste generator. The tank has been placed upon a 1952 truck chassis which is owned by the contract hauler. Normal haulage is 1,200 gallons per truckload, but state laws restrict the volume hauled in March, April, and May to 750 gallons per trip.

Hauling of spent acid usually occurs one day per week with 7-8 truckloads handled during a ten hour day. The contract hauler provides the truck and a driver at a rental rate of $17.00 per hour. The waste generator provides ten hours of labor per week (general maintenance labor) to help the driver load, dilute, and neutralize the spent acid.

A clay-lined storage pond is located on the farm adjacent to the land treatment area. It has a volume of 200,000 gallons, or an estimated storage capacity of 40 weeks. However, the storage pond has reportedly overflowed at least once. Wastes are placed in the storage pond when the adjacent field is not accessible for direct application of waste. The driver of the transport truck reportedly keeps track of waste application locations within the land cultivation site.

Typically, wastes are applied directly to the land cultivation site by the contract hauler. The tank truck is equipped with a valve leading to a six-inch stove pipe at the side of the truck. After the valve is opened, the truck is driven along on the site and the waste spreads over an approximately 15-foot wide area. Repeated applications are made in the same area for a period of several months. Seven or eight applications per day are made,

TABLE 1. SELECTED PHYSICAL/CHEMICAL CHARACTERISTICS OF THE SITE

Characteristics	Published Source*	Data From Site Visit/ Analysis**
I. Soil Conditions		
A. Soil Classification	Light silt loam to light silty clay loam	-
B. pH Characteristics	4.5-7.3	5.8-6.2 (control area)
C. Cation Exchange Capacity (meg/100g soil)	-	14.9-15.3 meg/ 100g soil (control area)
D. Soil Organic Content (or TOC)	-	TOC: 0.6% dry solids (control area)
E. Water Retention Ability	a) Available water capacity: 8 to 12 inches available water (to 5 feet) b) Permeability: well drained	-
II. Ground & Surface Water Proximity		
A. Surface Water	Stream located 1/2 to 1-1/2 miles down the hill, to north	Same
B. Ground Water	Area's mean well depth >450 feet	(Resident farmer's well at 200')
III. Topographic Conditions		
A. General Topography of Vicinity of Site	Gently sloping to steep upland and valley slopes	-
B. Topographic Relief of Area Visited	-	Site leveled to <5% on top of hill; area of rolling hills where some slopes may be as much as 30%
IV. Meteorological Conditions		
A. Average Yearly Precipitation	∿30 inches (40% in summer)	
B. Frost Free Period	∿150 days	
C. Maximum Temperature	∿83°F (July average)	

*Includes information from Soil Conservation Service Personnel & Publications, USGS Surveys, State & University Surveys, and/or ref. 14, 22.
**Includes Arthur D. Little, Inc. observations and analyses from site visits, as well as interviews with facility personnel and representatives of waste generators and farms.

separated by a week of inactivity during which drying occurs. In wet periods, a spring tooth cultivator, drawn by a tractor, may be used to hasten the drying process and incorporate the waste to a 4-5 inch depth. The mixing frequency is approximately 3 times per year. Other than this, there is no effort made to incorporate the waste into the soil during the active application period.

Wastes that are placed in the storage pond are periodically removed by a drag line and allowed to dry on the perimeter of the application area before being spread by a bulldozer. It appears likely that wastes may be unevenly applied by these procedures, making the application rate estimates over any area uncertain.

State regulations require that lime and phosphate be applied to the land periodically depending upon the results obtained by monitoring the soil. During 1977, 120 tons of lime were applied to the site by a contract applicator. Annually, 1,200 pounds of 42% phosphate per acre is required to be applied to the site. Such activities must be kept in mind in any interpretation of the results of program sampling efforts.

Land Treatment Management

Coordination of disposal activities at the site is highly informal. The waste generator's role has been one of setting up the waste disposal operation which includes contracting for hauling and liming activities. Once waste is at the site, either applied to the field or in the storage pond, all additional activities are taken care of by the site owner. Table 2 summarizes the responsibility for activities surrounding the land treatment operation at this site.

Monitoring

Monitoring of the land treatment activity at this site was required by state regulatory authority. The soil waste mixture is monitored three times a year for pH amendment requirements. This is usually in May, August, and October. Lysimeters have also been placed at several locations on the site, although the ones placed in the storage pond cannot be monitored because they are reportedly covered by waste and/or are inaccessible. The waste generator is responsible for all monitoring activities which include waste content and the required on-site monitoring. Monitoring procedures are summarized below:

- Waste: pH - each truckload; pH, water, total solids, Fe, Zn, Pb and specific conductance - once a month.
- Soil: pH - 3 times a year to determine lime addition requirements.
- Water: Lysimeters are in several locations at the site.

TABLE 2. SITE MANAGEMENT AND RESPONSIBILITY

	Plans/Decides Manages/Supervises	Performs	Approves
Storage	W.G.	LCSO	W.G.
Pretreatment	W.G.	W.G.	W.G
Waste Mixing	None		
Transport	W.G.	C.H.	
Application	W.G./LCSO	C.H.	
Soil Incorporation	LCSO		
Soil Waste-Amendments	W.G.	C	
Farming	None		
Monitoring	W.G.	W.G.	W.G.

W.G. = Waste Generator

LCSO = Land Cultivation Site Owner/Farmer

C.H. = Contract Hauler

C = Contractor

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

In sharp contrast to other land disposal options, land treatment can be managed so that the waste application area need not be irreversibly removed from any other potential practical usage. The basic reason is that plant-soil systems have a natural assimilative capacity for waste constituents. If rates and total quantities of wastes applied are controlled so that the assimilation capacity of the site is not exceeded dor any constituent of the waste, no potential future use of the site will be precluded. Assimilative capacity is both chemical specific and site specific. In other words, each chemical constituent of a given waste will be assimilated to a different extent at the same site; and the same chemical constituents will be assimilated differently at different sites.

The conclusions of the present study are limited to the environmental acceptability of land treatment for lime neutralized sulfuric acid pickling liquor sludge from one particular ferrous metal parts manufacturing plant, at one particular application site. The results cannot be generalized, either to neutralized pickling liquor sludges from other plants in the ferrous metal fabrication industry, or to other potential land treatment sites for the particular neutralized pickling liquor sludge investigated. The field study findings do provide insight into the factors that should be considered in the design and operation of a land treatment site to ensure environmental acceptability. The field study results characterize, to the extent possible, actual practices at a land treatment site used for purposes of waste treatment rather than for purposes of research. Conditions of waste application were therefore given, and not under the control of the investigators.

CONCLUSION

The neutralized waste sulfuric acid pickle liquor sludge as applied contained about 20% solids and 80% water. Approximately 600,000 gallons/year had been applied over a 4 acre site every year for 5 years prior to field sampling. The most recent application had been one day before the sampling visit.

Of the metals analyzed", calcium, sodium and zinc were found in significantly hgher concentrations in the application area than in the control area. The measured zinc concentration in the upper six inches of soil was 93 g/g or 230 kg/ha. This is approaching the assimulative capacity of 500 kg/ha for soils with moderate CEC**.

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*As, B, Ca, Cd, Cr, Cu, K, Mg, Mo, Na, Ni, P, Pb, Se, V, Zn

**M. Overcash and D. Pal, "Design of Land Treatment Systems for Industrial Wastes," Ann Arbor Science, Michigan (1979).

The measured soil pH in the application area was about 3.6, as compared to 6.0 in the control area. The waste is neutralized with lime to pH 9 or above prior to application. The site is also monitored for pH, and additional lime is mixed into the soil periodically. Nonetheless, highly acid conditions persist probably due to oxidation of ferrous iron, a principal constituent of the waste. The acid conditions are unfavorable to immobilization of heavy metals.

Electrical conductivity and sulfate concentrations were much higher in the application area than in the control area. The results are indicative of sodium and calcium migration as soluble sulfates.

Surface run-off appears to be a problem at this site. The site is located on a mechanically leveled hill top. Berms and terraces have been constructed to prevent downhill erosion. However, evidence of erosion indicates the measures have not been fully effective. In addition, a waste storage lagoon has overflowed its containment berms in the past. Because the site is not in close proximity to surface water it is not likely that run-off will contaminate surface waters. However, run-off may effect agricultural land adjacent to the site by lowering soil pH and increasing availability of metals for plant uptake.

A high potential for pollutant migration from the site exists. The waste/soil mixture is acidic and could promote the migration of acid soluble metals. However, groundwater is located 200 feet below the site surface. Therefore, it is not clear if the potential migration would have a significant impact on area groundwater.

The landfarm owner indicated that he intended to return the site to agricultural use in the future. This action would require substantial reclamation of the site. The high concentrations of iron and the persistent low pH conditions due to the iron chemistry could render the site unsuitable for future agricultural purposes.

RECOMMENDATIONS

Future actions at the site should include:

- Investigation of the low pH conditions;
- Improvement of record keeping practices;
- Elimination of overflows from the waste storage lagoon; and
- Development of a post closure plan.

SECTION 3

APPROACH

DATA COLLECTION AND ANALYSIS

Samples of the waste, baseline soil, and soil/waste mixtures were collected and analyzed for inorganic constituents and organic compound classes. Plants were collected and analysed to assess the extent of uptake of inorganic waste constituents.

The analytical protocol involved determining the following classical and inorganic waste parameters: pH, SO_4, and Cl^-, electrical conductivity (EC), cation exchange capacity (CEC), total organic carbon (TOC), total Kjeldahl nitrogen (TKN), As, B, Ca, Cd, Cr, Cu, K, Mg, Mo, Na, Ni, P, Pb, Se, V and Zn. Plasma emission spectroscopy and ion/chromatography were employed for inorganic species.

Analytical techniques employed for organic species included liquid chromatographic separation of organics into aliphatic, aromatic, and polar classes (LC-H, LC-A and LC-X, respectively), total chromatographic organics (TCO) and gravimetric (GRAV) analysis for volatile and non-volatile portions, and high resolution mass spectrometry (HRMS) for sorting classes by hydrogen saturation and heteroatom composition. The sampling and analytical methods are described in detail in the Appendix.

DATA INTERPRETATION

The analytical results from sampling the waste, the site receiving the waste, and a control site were compared to assess, insofar as possible, the relative decomposition, accumulation and migration of inorganic constituents and organic compound classes. The sampling and analytical program used in this study was designed to include sampling and analysis of appropriate control areas at the site so that any apparent concentration changes of waste components in application area samples could be differentiated from background levels. However, during preliminary site visits several factors were identified which would make it difficult to interpret any observed, apparent concentration changes. These factors include the following: an ideal control area was not available at the site; and, the chemical compositions of applied wastes were known to have varied over time.

The existence of many significant sources of uncertainty in the background data on the site made it desirable to provide some additional checks on the validity of the analytical data besides that provided by comparison of

TABLE 3. COMPARISON OF "TYPICAL" ELEMENTAL CONCENTRATION RANGES IN SOILS AND PLANTS WITH CORRESPONDING CONCENTRATION RANGES IN CONTROL AREAS USED IN THIS STUDY

Element	Typical Mean ppm Dry Soil (Range)[1]	Range ppm Dry Soil This Study[2]	Typical Range ppm Dry Plant Wt. Basis	Range ppm in Plant Ash This Study[5]
As	6 (0.1-40)	0.8-16	0.1-5[3]	1-16
B	10 (2-100)	2.1-9.2	5-30[3]	31-620
C	20,000	6,000-29,200	--	--
Ca	13,700 (7,000-50,000)	2,200-13,00	1,000-20,000	23,000-171,000
Cd	0.06 (0.01-0.7)	.3-.7	0.2-0.8[3]	1-4
Cr	100 (5-3,000)	7.9-65	0.2-1[3]	19-140
Cu	20 (2-100)	11-41	4-15[3]	69-290
K	14,000 (400-30,000)	2,300-8,400	20,400[4]	26,000-54,000
Mg	5,000 (600-6,000)	4,000-6,000	500-15,000[4]	14,000-40,000
Mo	2 (0.2-5)	1.7-3.3	0.2-5[3]	14-64
N	1,000 (200-2,500)	464-1,700	--	--
Na	6,300 (750-7,500)	22-440	--	940-10,000
Ni	40 (10-1,000)	9.6-31	10-10,000[4]	7-36
P	650	5,300-10,000	1,000-10,000[4]	17,000-168,000
Pb	10 (2-200)	24-280	0.1-10[3]	29-370
Se	7 (10-25)	0.1-0.5	0.1-2.0[3]	<.1-0.5
V	100 (20-300)	17-50	20-500[3]	3-90
Zn	50 (10-300)	41-110	10-300[3]	270-3,800

1. Bowen, H.G.M., Trace Elements in Biochemistry, Academic Press, Inc., NY, 1966.
2. CTL 0-6" Samples.
3. Allaway, W.H., Agronomic Controls Over the Environmental Cycling of Elements.
4. Berger, K.C., Sun Soil and Survival, University of Oklahoma Press, OK, 1976.
5. CTL Samples.

control and application area sample results. These checks are described below:

Inorganic Analysis

Validation of Control Samples --

The analytical data obtained in this study for control area samples from six land treatment sites are compared in Table 3 to typical concentration ranges found in soils and plants. Comparison of the soils data for the six sites indicates that almost all of the results obtained in this study are within typical concentration ranges. Exceptions are phosphorus (P), which was generally found in concentrations in excess of typical ranges, and sodium (Na) and selenium (Se), which were generally found in concentrations less than typical ranges. The selenium discrepancy may be due to volatilization of that element during the sample preparation procedure used in this study; the reasons for the sodium and phosphorus differences are not clear. Comparison of data on plants is of limited utility for several reasons, viz.: 1) plant uptake is species-specific; 2) uptake by a particular species is dependent on soil conditions; and 3) for the purpose of this study, elemental concentrations in plants have been expressed on an ash weight basis to compensate for the frequently poor physical condition of plants collected in the field. However, if we assume that the ash weight is usually on the order of 10% of the dry weight (the actual mean ash weight for all six control area samples in this study was 8.7% of dry weight), then the majority of results obtained in this study lie within typical ranges encountered in plants on a dry weight basis. In general, comparison of the results for control area samples in this study to typical elemental concentrations ranges in soils and plants suggests that there are no severe biases which would invalidate conclusions from the analytical data presented in this report.

Total Mass of Analyzed Parameters --

The sum of the masses of individual analyzed species in a sample of waste is a fraction of the total waste mass. For instance, if there were no species in the waste solids other than those determined in this study, the sum of all the individual masses should be approximately equal to 100%, depending on the uncertainty associated with the sampling and analytical methods. Inspection of the data presented shows that species determined in this study account for 68% of waste weight. The significance of this observation depends, of course, on the identity of the species that were not determined. Likely candidates are the elements Fe, H, O, Si and Al, all of which could be reasonably expected to occur in significant quantities in wastes of the type included in this study. In any case, consideration should be given to the presence of possibly substantial amounts of unidentified species in subsequent interpretations of the analytical data presented in this report.

Definition of Significant Pollutant Increases --

Interpretation requires some judgment about what constitutes a significant change in concentration of a given parameter relative to background levels. To this end, the results for total metals, Total Organic Carbon (TOC), and Total Kjelkahl Nitrogen (TKN), were expressed as ratios of total concentration in the application area to total concentration in the control area (APN/CTL).

Inspection of the data generated from six landfarm sites indicates that three elements - K, Mg, and P - show no significant increases above background, i.e., individual APN/CTL ratios for each of the elements at each site are close to 1.0 indicating that there is little difference in the actual concentrations of each of the elements between the APN and CTL area samples. The relative standard deviations of the mean APN/CTL ratios for these three elements are 33% (K), 9.1% (Mg), and 20% (P). Their mean relative standard deviation is approximately 20%; this number may provide a useful measure of the background variability of elemental concentrations in soils. Thus, for the purpose of this report, it has been assumed that a significant change relative to background levels is indicated by a difference in the mean APN area concentration of more than $\pm$20% relative to the mean CTL area concentration (i.e., APN/CTL > 1.2).

The results for total metals, TOC and TKN in the wastes from all sites were used along with data obtained from the site owner on waste application rate (i.e., kg waste/acre/yr.) and waste percent solids, to estimate the number of years before one could expect to observe any increase of the elements analyzed in this study. The following assumptions were made:

1. Actual application rates have been the same as those given by the site operator;

2. All the waste generated for land treatment has been applied to the area which we sampled;

3. The waste has been incorporated uniformly into the top 12" of soil over the entire area described in #2; and

4. The waste composition has been constant and identical to that determined in this study.

The resulting estimates are discussed in more detail in chapter 4.

The steps in the procedure used to calculate the years of waste application necessary before one could expect to observe any increase above background were as follows.

Waste Application Rate --

The quantity kilograms of waste solids/acre/year was calculated from data supplied by the waste generator. For certain sites, the waste generator was able to provide an estimate of this quantity directly for other sites, where perhaps only an estimate of the annual volumetric waste generation rate was available, this calculation was performed according to the following equation:

$$\text{Kilograms of waste solids/acre/year} = \frac{\text{Annual volumetric mean generation} \times \text{Density of waste as applied} \times \text{\% solids in waste}}{\text{Acres of application area}}$$

In those cases where estimates of the waste density and % solids were not available from the waste generator, values obtained from laboratory analysis of waste samples collected during sampling visits to each site were used. As indicated in assumption 2 above, the value of the quantity "acres of application area" in the above equation was equal to the area in acres of the waste application area sampled in this study.

Annual Leading Rate of Individual Waste Species --

The quantity "kilograms of waste solids/acre/year" calculated in Step 1 was multiplied by the concentration in ppm of the element of interest determined in this study in waste samples collected from each site to give the annual loading of that element:

kg/acre/year x mg/kg (=ppm) of element of interest in waste solids = mg/acre/year

According to assumption 3, the waste was assumed to be incorporated uniformly into the top 12 inches of soil over the entire application area so the units of this quantity were assumed to be equal to mg/acre-foot/yr.

Annual Increase of Individual Waste Species --

The annual loading expressed as mg/acre/yr of each element of interest obtained in Step 2 was divided by an estimate of the average mass of one acre-foot of soil to give the predicted annual increase in concentration of each element of interest.*

Estimated Years of Waste Application --

The predicted annual increase in concentration of each element of interest was used to estimate the years of waste application necessary before one could expect to observe any increase above background of the elements analyzed in this study. The latter quantity depends on the detection limits of the sampling and analytical methods used for each element of interest. For example, the atomic absorption spectroscopic procedures used for analysis of many of the elements determined in this study involved digestion of ~1.5 g of soil and dilution of the resulting solution to 50 milliliters. Assuming that our instrumental method was capabile of detecting a change in concentration

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[The average mass of one acre-foot of soil was calculated as follows:

1 acre ~ 43,560 ft^2; 1 acre-foot =
43,560 ft^3 x 1 ft = 43,560 ft^3;
43,560 ft^3 x .0283 m^3/ft^3 = 1233 m^3;
average bulk density = 1.6 g/cm^3 = 1.6 x 10^3 kg/m^3 (cf. Overcash, M.R. and D. Pal, Design of Land Treatment Systems for Industrial Wastes Theory and Practice, Ann Arbor Science, 1979);
1233 m^3 (1.6 x 10^3 kg/m^3) = 2 x 10^6 kg
Therefore,
(mg/acre-foot/yr) ≃ 2 x 10^6 kg/acre-foot $\frac{\text{mg of element of interest ppm)}}{\text{kg of soil-year}}$ $\frac{}{\text{year}}$

of the element of interest in that solution equal to 1 part per million, the corresponding concentration change of that element in the soil sample taken for analysis would be ∿ 30 parts per million:

$$\left(\frac{1\mu g}{mL} \times 50\ mL\right) / 1.5\ g \simeq 30\mu g/g = 30\ ppm\ in\ soil$$

The quantity ppm/year calculated in Step 3 was divided by 30 ppm to give the number of years of waste application necessary to observe a concentration change. Note that the "observable concentration changes" referred to here are not the same as "significant concentration increases" referred to in the preceding discussion.

For most elements determined in this study by atomic absorption (AA), the actual instrumental detection limit is probably lower than 1 ppm. However, since a systematic study of the detection limits of the combined sampling and analytical methods was beyond the scope of this study, the 1 ppm estimate may, in fact, be a more reliable estimate of the actual detection limits, given the uncertainty associated with the sampling methods.

Organic Data Interpretation

The principal objective of the organic chemical analysis program was to obtain data for a preliminary evaluation of the effectiveness of land treatment in degrading organic components of chemical wastes. To accomplish this objective it was necessary to characterize the organic components of the waste and to look for evidence of significant accumulation, degradation or migration of those components in the soil.

The organic analysis scheme provided for quantitative analysis of extractable volatile (TCO) and non-volatile (GRAV) organics, and of three polarity classes (LC-H, LC-A and LC-X) by liquid chromatography. Qualitative analysis of the organics by compound type was achieved by HRMS which provided data on heteroatom composition and the degree of compound saturation (R + DB values).

The combined qualitative and quantitative results provide insight into the extent of waste component degradation. For instance, an increase in polar species in APN area samples can be taken as an indication that the aromatic and aliphatic constituents originally in the waste have partially degraded since the byproducts of aerobic oxidation are generally polar oxygenated species. Typically, the organic analysis results do not permit determination of which waste components are being transformed into particular types of degradation products. However, the HRMS data do indicate which specific classes tend to persit in the soil column and which classes tend to appear as degradation products.

Accumulation of certain waste types can be determined by increases of aromatic and aliphatic classes relative to each other. For example, suppose the LC-H and LC-A fractions of extractable organics account for more than 50% of the organics in the APN 0-6 and 6-12 layers and in the control soil in

these fractions are only 10% of the total. The ratio of LC-A to LC-H in the waste is 0.24; in APN 0-6, 0.37 and in APN 6-12, 0.96. The absolute values of the LC-H and LC-A concentrations were lower in the APN 6-12 than in the 0-6. These types of trends are indicative of 1) preferentially degradation/or loss of aliphatic waste constituents over that of aromatic hydrocarbons, and 2) of aliphatic waste constituents over that of aromatic hydrocarbons, and 2) in the APN soil compared to the CTL soil, without the appearance of oxidative degradation.

SECTION 4

RESULTS AND DISCUSSION

WASTE AND SOIL ANALYSIS

The results of analysis for total metals, TOC and TKN, in the wastes applied to this site are presented in Table 4. These data were used along with data from the waste generator on waste application rate (6×10^5 gal/ year over a 4 acre site), waste density as applied (11 lbs/gal) and percent solids (20%), to calculate an estimate of the years of waste application necessary before one could expect to observe any increase above background of the elements in Table 4. We believe that the validity of these assumptions at the site is lowered because of irregular application and incorporation methods. Based on the above, observable increases of elements in soils at the time of sampling would be expected for Ca, K, P, Mg, and C (in decreasing order of predicted concentration). Table 4 illustrates this prediction.

Inorganic analytical data on soils is presented in Table 5. To assess significant changes with respect to background, results for metals, Total Organic Carbon (TOC) and Total Kjeldahl Nitrogen (TKN) were expressed as ratios of total concentration in application area to total concentration in control area. Soil samples taken at the site to represent controls were taken from the berms at the site. While these berms were constructed of site material at the time the site was constructed, it is not possible to assume that soil conditions are the same as those in the application area. These less than satisfactory control conditions should be kept in mind when evaluating the data and drawing conclusions. As discussed in Appendix A, for the purpose of this report, it was judged that a significant change relative to background levels is indicated by a difference in the mean APN area concentration of more than 20% relative to the mean CTL area concentration (i.e., APN/CTL> 1.2).

Ca is present at higher concentrations in the application area soils than in the controls, as predicted. A number of other elements--B, C, Cd, Cr, Mo, N, Na, and Zn--also have APN/CTL ratios > 1.2. For B, Cd, Cr, and Mo the absolute concentrations are small and the apparent increase may not be significant. The calculated and observed concentration changes for the other elements are shown in Table 6. All of these elements show concentration increases greater than those predicted, which suggests that the application rate was greater than estimated, or that the area to which the waste was applied was less than estimated. The relative increases in Ca, Na, and Zn appear to be consistent with each other and with that conclusion. However, there is no apparent explanation for the substantial increases in TOC and TKN in the application area. It may be that these increases have resulted from some present or prior activity in the vicinity of the site not connected with this waste

TABLE 4. INORGANIC WASTE ANALYSIS AND ESTIMATED YEARS FOR OBSERVABLE SOIL CONCENTRATION

Element	Waste Concentration (ug/g dried solids)	Estimated Years of Waste Application for Observable Soil Concentration Change
As	0.2	*
B	26	*
C	0.12%	1
Ca	3.6%	1
Cd	1	*
Cr	110	4
Cu	92	4
K	1800	1
Mg	1400	1
Mo	7	*
N	40	*
Na	92	4
Ni	30	*
P	2.2%	1
Pb	26	*
Se	0.1	*
V	5	*
Zn	12	*

*greater than 10 years

TABLE 5. INORGANIC WASTE ANALYSIS OF CONTROL AND APPLICATION SOILS

Element	Concentration in Soils (µg/g dry wt.) CTL 0-6"	CTL 6-12"	APN 0-6"	APN 6-12"	APN/CTL*
As	2	3	2	2	0.8
B	5	7	10	6	1.3
TOC	0.6%	NA	0.83%	NA	1.4
Ca	2300	2200	18000	11000	6.4
Cd	0.3	0.3	0.7	0.6	2.2
Cr	38	41	59	53	1.4
Cu	25	25	21	23	0.9
K	3000	3300	3200	2900	1.0
Mg	4000	4300	5200	4600	1.2
Mo	2.3	2.0	4.6	3.6	1.9
TKN	779	NA	10000	NA	12.8
Na	100	130	220	200	1.8
Ni	21	23	20	22	1.0
P	6900	7200	8500	7100	1.1
Pb	24	21	22	22	1.0
Se	0.1	0.1	0.1	0.1	1.0
V	17	19	12	18	0.8
Zn	60	54	93	110	1.8

NA = Not Analyzed
* = APN/CTL Ratio calculated as $\{APN(0-6)+APN(6-12)\}/\{CTL(0-6)+CTL(6-12)\}$

TABLE 6. CALCULATED AND OBSERVED CONCENTRATION CHANGES IN THE SITE AREA SOILS

	Element				
	C	Ca	N	Na	Zn
Calculated[1]	+ 90	+0.3%	3	7	+ 1
Observed[2]	+1150	+1.2%	0.5%	95	+45

1. Calculated concentration change =

$$\frac{[(\text{Kg solids/acre/yr.}) \times (\text{ppm of element in waste})]}{2 \times 10^6 \text{ kg soil/acre ft.}}$$

2. Observed mean concentration change =

$$\frac{[(\text{ppm}_{\text{APN 0-6" + APN 6-12"}} - (\text{ppm}_{\text{CTL 0-6" + CTL 6-12"}})]}{2}$$

disposal operation. Comparison of the concentrations of Ca, Na, and Zn in APN 0-6" and APN 6-12" soil samples indicates that the concentrations of each of these elements are higher than in the corresponding CTL samples and are quite similar in both samples.

Data for pH, CEC, sulfate, chloride, and electrical conductivity are given in Table 7. The significantly elevated levels in electrical conductivity and SO_4 in the APN area samples suggests that the Na and Ca may be present as soluble sulfates. Expressing the Ca and SO_4 concentrations in units of millequivalents indicates that these two species are, in fact, present in a stoichiometric ratio close to that expected for $CaSO_4$.

PLANT ANALYSIS

The results of analyses of plant samples collected at the site are summarized in Table 8. At the site, plants were not growing on the application area. Because discing operations at the site would turn under any plants which might have grown there, it is not clear if the soil was capable of supporting plant growth. In order to attempt comparisons of measured levels with those reported in the literature, agricultural escapes in the legume family were sampled from the edges of the application area. A true control area did not exist for this site and plants were sampled from a neighboring field below the hill where wastes were being applied.*

The above-ground portions of alfalfa, yellow clover, and red clover plants were collected from the edges of the application area. The alfalfa and red clover were not healthy looking specimens. This could be attributed to the effects of frost and/or the effect of runoff from the application area. Only red clover and alfalfa could be located in the control field. These specimens were in much better condition, but were also protected from winds by the hill above.

Most of the discussion presented here focuses on the alfalfa samples collected because the application area red clover were in particularly bad shape (note the percent ash in Table 10) and yellow clover was not present in the area utilized for control plants. Levels of chromium, copper, nickel, and lead appear elevated above levels in alfalfa collected from the control area. Ratios of application area plant levels to control plant levels for these same elements also indicate considerable increases. Zinc, selenium, molybdenum, phosphorus, and sodium appear similarly elevated when compared with control areas. Application area soil levels of these constituents and waste levels do not appear similarly high. The lowering of pH levels to below 4 is probably a significant effect of waste application at this site. The application area is reportedly limed, but the oxidation processes associated with the ferrous iron content of this waste are likely to be responsible for the lowered soil pH.

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* Plants at the edge of the application area and berms used for soil control samples were not the same species as those from the "control" area below the hill.

TABLE 7. SITE SOILS: INORGANIC PARAMETERS

Sample	pH	C.E.C. me/100g	E.C. μmhos	$SO_{4}^{=}$ μg/g	Cl^{-} μg/g
Waste				35.0%	9
Soil:					
CTL 0-6	6.2	15.3	205	320	3
CTL 6-12	5.8	14.9	290	320	6
APN 0-6	3.8	12.0	4600	5.2%	16
APN 6-12	3.4	10.4	4100	2.4%	9
APN/CTL		0.7	176	118	28

TABLE 8. PLANT SAMPLE CONTENT OF TOTAL ELEMENTS AS ANALYZED IN ASHED SAMPLES

	Concentration (ug/g)						
	Alfalfa			Red Clover			Yellow Sweet Clover
Element	CTL	APN	APN/CTL Ratio	CTL	APN	APN/CTL Ratio	APN
% Ash	9.8	7.6		7.9	23.1		5.9
As	2	2	1.0	1	8	8	4
B	540	630	1.2	430	78	0.2	370
Ca	17.1%	18.0%	1.0	13.7%	4.5%	0.3	13.4%
Cd	--	3	--	1	1	1.0	5
Cr	37	240	6.5	38	93	2.4	57
Cu	190	470	2.5	290	120	0.4	245
K	3.9%	5.7%	1.5	5.4%	1.0%	0.2	5.6%
Mg	2.8%	4.7%	1.7	3.6%	1.4%	0.4	4.5%
Mo	23	48	2.1	31	9	0.3	22
Na	4500	1.5%	3.3	9600	2300	0.2	6300
Ni	23	100	4.3	36	35	1.0	50
P	2.5%	7.6%	3.0	3.4%	1.7%	0.5	2.2%
Pb	120	175	1.5	100	43	0.4	160
Se	<.2	<.5		<.1	<.1		<.1
V	89	24	0.3	17	53	3.1	90
Zn	270	590	2.2	390	230	0.6	610

Although control soil and plant samples cannot be compared due to differences in areas sampled, several observations concerning analyses of plant levels of constituents can be made:

- Lowered soil pH increases the availability of some metal species; chromium, copper, nickel, lead, and zinc, for example, are likely to be more available under such soil conditions and plant levels could well be a reflection of such conditions.

- Soil levels of chromium, copper, nickel, and zinc in the application area are not proportionately elevated compared with plant samples. It is conceivable that leaching and uptake could explain such discrepancies, but such a conclusion is very tenuous based on a single sampling effort. It is also conceivable that reported waste holding pond overflows on the site could influence the availability of metals for plant uptake.

It is curious that measurements of extractable metals (Table 9) from the application area do not reflect the heavy metal elevations found in plants bordering it except for slight increases in boron. Further, it is interesting to note apparent increases in application area alfalfa levels of boron, chromium, copper, nickel, and molybdenum although soil levels are not similarly elevated, and that the yellow clover samples do not indicate element levels as high as the other two species collected. These plants were growing at a greater distance from the application area than the red clover and alfalfa. Species variation must also be considered. Again, a significant observation at this site is the apparent effect of low soil pH on levels of certain constituents in plants sampled.

POTENTIAL ENVIRONMENTAL IMPACT

Ground and Surface Water

Potential environmental impacts of the land treatment operation due to direct contact or migration of waste are discussed below.

Because groundwater is located well below the surface, direct contact between waste and groundwater appears unlikely. Surface water runoff containing waste is a likely occurrence at this site. Although berms have been constructed and slopes terraced to minimize runoff, erosion gullies observed at the site indicate these measures have not been totally effective. In addition, reports indicate that the waste holding poind has overflowed on occasion. However, the nearest surface water body is at least a half mile away. Given the distance and the fact that the area is heavily vegetated, direct contact between significant amounts of waste and surface water bodies appears to be of small likelihood.

Food Chain

Based on the alfalfa plant analyses which indicate that lowered pH is effecting uptake of waste material from the soil, a number of questions concerning food web implications arise:

TABLE 9. SOIL SAMPLES: DTPA EXTRACTABLE METAL

Element	Concentration in Soils (μg/g) CTL 0-6"	CTL 6-12"	APN 0-6"	APN 6-12"	APN/CTL*
As	NA	NA	NA	NA	-
B	0.1	0.2	0.3	0.3	1.6
Ca	NA	NA	NA	NA	-
Cd	<0.1	<0.1	<0.1	<0.1	1.0
Cr	0.1	<0.1	<0.1	<0.1	1.0
Cu	0.1	0.2	0.1	0.1	0.7
K	120	89	65	47	0.5
Mg	140	110	560	310	3.5
Mo	<0.1	<0.1	<0.1	<0.1	1.0
Na	9	11	35	18	2.6
Ni	2	2	1	1	0.5
P	54	46	72	70	1.4
Pb	NA	NA	NA	NA	-
Se	NA	NA	NA	NA	
V	0.3	0.1	<0.1	<0.1	<0.5
Zn	3	2	1	3	0.8

NA = Not Analyzed

* = APN/CTL Ratio is calculated as

$$\{APN(0-6)+APN(6-12)\}/\{CTL(0-6)+CTL(6-12)\}$$

(a) Do the results reflect an equilibrium level of removal of the above mentioned waste components or will increased application cause increased concentrations? Further, to what extent will migration limit the availability of these constituents to plants?

(b) Are concentrations in plants on the site sufficiently high and available to have adverse effects on fauna that regularly feed on those plants?

This site is located in a rural area at the top of a hill. Wildlife access to the site is unrestricted by manmade barriers but requires a steep ascent from the adjacent agricultural areas and early-successional deciduous woodlands. Because of this ascent requirement, the relative absence of permanent vegetation on the site and the frequency of human activity on the site and adjoining municipal solid waste landfill, it is considered unlikely that the region's larger terrestrial herbivores (e.g., deer) make significant, if any, use of the site. Rodents, other omnivores (e.g., skunks, racoons), predators such as foxes or feral cats/dogs, insects, and a diverse representation of the region's terrestrial birds, are likely users of the site. Much of the wildlife utilization of the site can be attributed to the attraction provided by the adjacent municipal solid waste disposal activity.

The small waste storage lagoon on the site showed no evidence of supporting any permanent aquatic fauna during a June visit, when a relatively great standing crop would be expected. Limited use of the lagoon by water-dependent birds and herpetefauna appears possible.

This site appears to afford considerable opportunity for direct waste/wildlife interactions, but mostly for species of little or no commercial/recreational importance and of limited geographic range. Site "food web" species linked to man include mourning dove, pheasant and, potentially, abbit. It is considered unlikely that rabbit or pheasant from this site would be subject to hunting pressure beyond any exerted by the site owner. However, migratory mourning doves may use the site and subsequently be hunted and consumed off site. The quality of the standing water in the waste holding lagoon was not measured. Levels of iron, known to be high in the waste, were also not determined in the application area. Nonetheless, there is presently no empirical basis for expecting adverse faunal impacts of local or regional significance.

Agricultural Soil

While the site is located in an agricultural region, its hilltop location and proximity to the local municipal landfill make the degree to which it would be utilized for agricultural purposes in the future unclear. Nonetheless, it would appear from the low pH measured in this sampling effort and the amount of waste being applied that, in spite of the required liming and fertilizer additions, significant reclamation would be required for future agronomic production at this location. It must also be noted that considering that iron is in the waste in potentially significant quantities and was not measured as part of this program, it is not clear to what degree the amounts being applied would have an adverse affect on future use of this site for other than disposal.

Migration

Migration of pollutants to groundwater is a potential problem at this site. The potential for soils of this area to attenuate heavy metals such as copper, zinc, etc., appears to be moderate. This is based on analyses from this program of the chosen control area soils, which may not be totally representative of soils in the application area.

Analyses of soils from the application area show greater concentrations than predicted for elements that were expected to increase due to waste incorporation and suggest application rates greater (or application areas smaller) than those used in these estimations. Levels of constituents such as sodium, copper, and zinc are elevated above control samples in both the 0-6" and 6-12" samples. There is no basis for judging how much downward migration of these constituents may have occurred, due to the irregularity of the application procedures.

Dramatic lowering of soil pH due to waste application is of particular concern at this site. The groundwater impact potential of this situation may not be as significant as might first appear because the wastes evidently do not contain large amounts of acid-mobile constituents that we analyzed for. However, migration of some constituents (zinc and copper are examples) appears quite possible. It would also appear that movement of soluble salts would be of concern, considering the waste composition. Further, there are elements that are likely to be present in significant amounts in the waste (iron) that have not been analyzed in this program, so conclusions cannot be drawn about their mobility under these circumstances. Certainly, questions remain concerning the significance, if any, of the amounts of constituents that may be migrating from the site.

APPENDIX

METHODS OF SAMPLING AND ANALYSIS

DATA COLLECTION PROCEDURES

Several approaches were used to collect data from the six field sites selected for study. Information sources included published surveys such as those produced by the Soil Conservation Service and/or local universities and state agencies. Where feasible, information gathered from interviews with site or industry personnel along with site observations were utilized to confirm or adjust such information for location specificity.

FIELD SAMPLING

The field sampling and analysis program was designed to provide information on the following:

1. The rate and extent of waste degradation,
2. The migration of inorganic species,
3. The accumulation of waste constituents in the soil, and
4. Bioaccumulation of inorganic species in vegetation.

To this end, measurements were made of the concentration of various chemical species in soil and vegetation samples taken from waste application and control areas. The species selected for analysis were those that occur as a direct result of the land cultivation operation and/or transport of any constituents of the wastes.

Sampling Methods

Sampling Locations--

At each site, samples were taken from (1) the area where waste had been applied and (2) the best identifiable control area. The ideal control area would have been upwind and upgradient of the waste application area, but in all other respects would have been identical to that area except that no waste had been applied. Selection of an appropriate control area was a problem at the majority of sites for a variety of reasons. In general, the design and operation of most sites did not include provision for a bona fide control area as described above. More specifically, problems included substantial variations in soil characteristics, drainage patterns and vegetation occurring within small distances; and uncertainty about the history of waste application outside the boundaries of the present application site. In all cases, a "control" area

was selected which necessitated the least compromise in the requirements stated above. In both control and application areas, samples were collected from a 4 x 4 grid covering the area. Wastes were collected from storage facilities or other sources, selected so as to assure that the samples were representative of the waste that was actually applied.

Sample Types--

The types and numbers of samples collected at each site included at a minimum the following:

	Control Area	Application Area
1) Waste	1 Sample	
2) Soil	2 Samples	2 Samples
3) Soil-Waste Mixture	--	2 Samples
4) Vegetation	1 Sample	1 Sample

Core samples of soil and soil-waste mixture were taken with a sampling tube. The resulting cores were 1" in diameter and 12" in length. These samples were divided in the field into two subsamples corresponding to 0-6" soil depth and 6-12" soil depth. Bulk samples were subsequently coned, quartered, and riffled to obtain amounts of sample appropriate for each analysis. Vegetation samples were collected from the same control and application areas from which soil samples were obtained. Unless noted otherwise, composite vegetation samples were prepared from whole plants minus roots. There were no opportunities for sampling surface water, runoff, or groundwater at any site during the sampling visits made.

CHEMICAL ANALYSIS

Inorganic

Analyses of inorganic parameters were conducted on the waste samples, soil and soil-waste mixture composite samples from application and control areas, and vegetation composite samples from application and control areas. Analytical methods used for determination of inorganic parameters are shown below. DTPA-Extractable metals are those metals which may be available for biological uptake.

Parameter	Method
B, Cu, Cd, Cr, Cu, K	HNO_3-$HClO_4$ digestion, plasma emission spectroscopy
Mg, Mo, Na, Ni, P, Pb, V, Zn	
As, Se	Hydride evolution, atomic absorption spectroscopy

Total Organic Carbon (TOC)	Combustion, gravimetric
Total Kjeldahl Nitrogen (TKN)	Digestion, distillation, volumetric
Sulfate	0.1 M LiCl extraction, ion chromatography
Chloride	H_2O extraction, volumetric $Hg(NO_3)_2$ titration
Cation Exchange Capacity (CEC)	Volumetric
Electrical Conductivity (EC)	Conductivity Meter
pH	pH Meter
DTPA-extractable metals	DTPA extraction, plasma emission spectroscopy

Organic

The organic analysis scheme is shown schematically in Figure 1. The methodology involved:

1. Solvent extraction with methylene chloride;
2. Quantitative analysis of volatile and non-volatile organics;
3. Liquid chromatographic separation of the extracts to divide the organics into three polarity classes: aliphatic hydrocarbons, aromatic hydrocarbons, and polar species; and
4. Qualitative analysis of organic compound classes present by high resolution mass spectrometry.

Each of the steps of the methodology is described in further detail below.

Extraction--

The method adopted for isolation of organic components from the waste and soil samples was extraction with methylene chloride. Methylene chloride is a solvent which gives high extraction efficiency for a wide range of organic compound types. In particular, it is generally effective for non-polar and moderately polar, hydrophobic organics, which are the types of compounds that dominate many current lists of compounds of concern. It should be recognized, however, that polymeric, humic, proteinaceous materials, very polar, water-soluble, or soil-bound species will not be efficiently extracted. It should also be noted that these non-extractable species, if isolated, would generally not be amenable to available analysis techniques. An organic compound which is extractable from a waste sample may not be extractable from a corresponding soil sample because of soil bonding. Since non-extractable organics are probably less likely to be transported into plant cells, they may be of less environmental concern.

Control and application area soil samples (ca 100 g) were Soxhlet extracted with methylene chloride (ca 200 mL) for 24 hours. Waste samples were

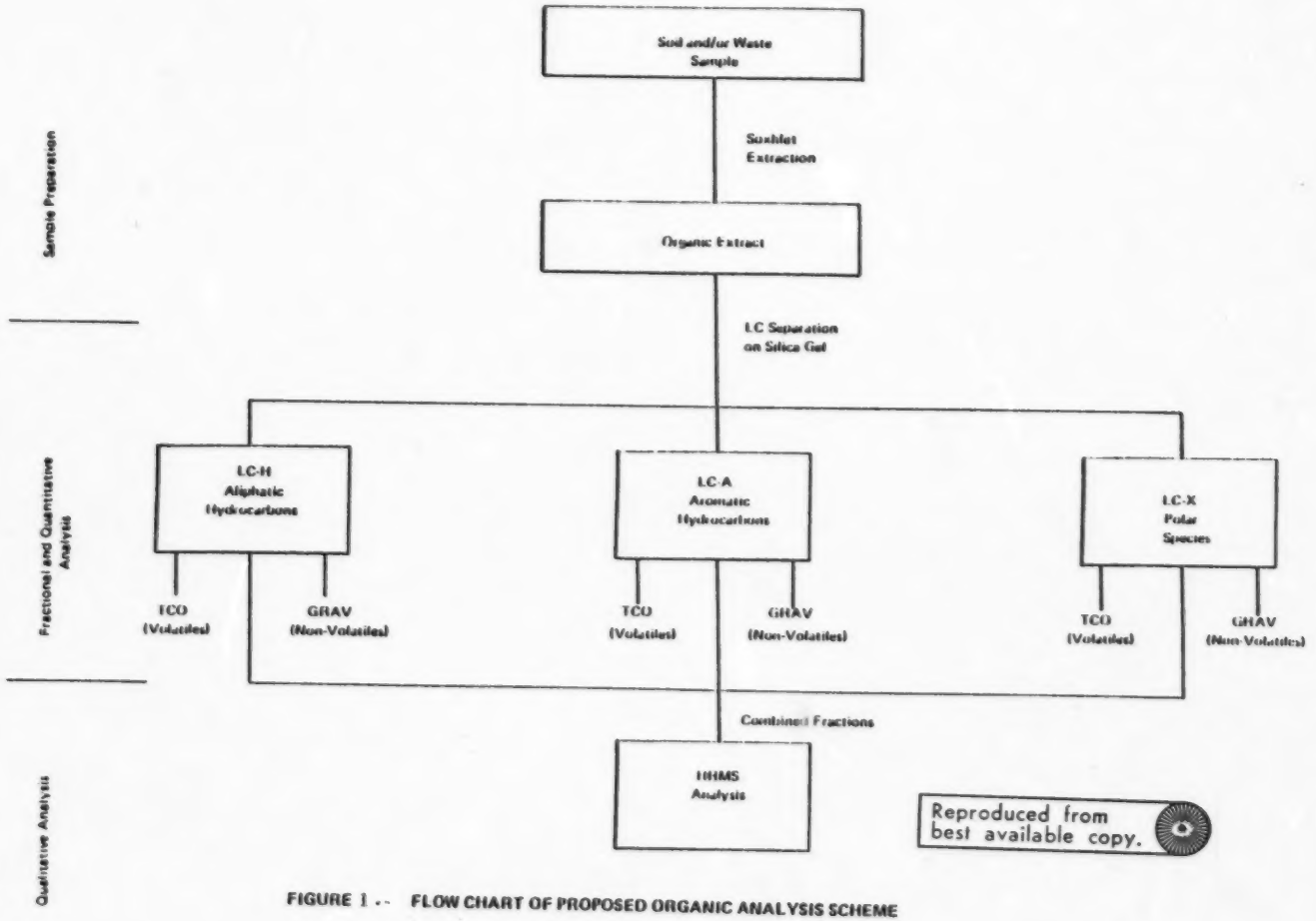

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FIGURE 1 -- FLOW CHART OF PROPOSED ORGANIC ANALYSIS SCHEME

subjected to Soxhlet extraction, or to liquid-liquid separatory funnel extraction (3 times 100 mL of solvent per liter of waste), depending on their physical state. The methylene chloride extracts were concentrated to 10 mL final volume by use of Kuderna-Danish evaporative concentrators.

Quantitative Analysis--

Total Chromatographable Organics (TCO)--The Total Chromatographable Organics (TCO) analysis is a gas chromatographic (GC) analysis procedure that uses a flame ionization detector. A 1-5μL aliquot of the sample is injected. Resolution of individual QC peaks is not intended. The total integrated detector response is used to derive a single estimate (mg) of the quantity of material in the 100-300°C boiling point range.* The detection limit for a complex sample mixture is on the order of 50 ppm (w/v) in the solution injected. This corresponds to 0.5 mg total in the 10 mL sample extract.

Gravimetric Analysis (GRAV)--The GRAV procedure is a quantitative analysis of non-volatile components (materials above 300° boiling point range) of the sample extract. An aliquot of the organic solution is evaporated to constant weight, over silica gel, in a tared weighing dish. The practical detection limit is on the order of 0.1 mg in the 1 mL sample taken for GRAV analysis. This corresponds to 1. mg total in the 10 mL sample extract.

Liquid Chromatographic Separation--

A liquid chromatographic (LC) separation on silica gel was used to separate the extracted organics according to polarity. This is a lowresolution technique that has been demonstrated at Arthur D. Little, Inc. to provide reliable separation of organic components into three classes as indicated below.

LC-H: Aliphatic Hydrocarbons

LC-A: Aromatic Hydrocarbons

LC-X: Polar Organics (oxygenates, amines, etc.)

Details of preparation of the silica gel LC column have been published. The methylene chloride extracts were applied to the column after solvent exchange into cyclohexane. The elution sequence used in this program was as follows:

LC-H: 15 mL of pentane

LC-A: 15 mL each, sequentially, of 20% methylene chloride in pentane; 50% methylene chloride in pentane; and methylene chloride

* Arthur D. Little, Inc., studies using model compounds have shown that n-hexadecane (b.p. 303 C) defines a reasonable break point between TCO and GRAV range materials.

LC-X: 5 mL each, sequentially, of 5% methanol in methylene chloride; 20% methanol in methylene chloride, and 50% methanol in methylene chloride.

Each fraction was analyzed by TCO and TRAV procedures as described above. The fractions were then recombined prior to HRMS analysis.

The LC procedure was originally scaled for 15-100 mg samples applied on column. However, the total amount of material available for some samples in this program was 10 mg. Quantitative recovery from the column was 70-100% when samples containing about 10 mg or more were used, but 50% for very small samples.

The reproducibility of the extraction and LC separation for these samples was checked by running duplicate LC columns on a site application area soil extract. The results are shown in Table 10.

High Resolution Mass Spectrometry--

High resolution mass spectra were obtained on the recombined LC fractions for each of the landfarm sample extracts. A Dupont (CEC) 21-110 B high resolution mass spectrometer, using a glass inlet and solids probe for sample introduction, was employed. Spectra were recorded on photoplates. The basic spectral data were then obtained by a photoplate reader and the position and intensity of the lines transferred directly to a laboratory data system (LDS). This is the HIRES output. The LDS, based on a Data General Elipse S/200 computer, was used for subsequent HRMS data processing.

The high resolution mass spectrometer is capable of measuring masses of ions in the spectrum with an accuracy of better than 0.001 atomic mass unit. Data from the HRMS analysis are reported to four decimal places in m/e (mass-to-charge ratio). The high accuracy and precision makes it possible to take advantage of the mass defect characteristics of atoms and use their exact masses to compute elemental composition assignments for the observed ions. The theoretical mass can be calculated for all "plausible" combinations of elements corresponding to a given mass. "Plausible" combinations are defined by the analyst, based on a preliminary manual examination of the HIRES data. The objective is to allow all of the elemental compositions (C + H; C + H + S; C + H + Cl, etc.) that are necessary to characterize the range of the sample chemistry, but to minimize the computation time and the number of incorrect, "near-miss" match assignments. The theoretical and measured masses are next compared and a "match" is identified when they agree to within a specified value, typically 0.002 or 0.003 atomic mass units. This information constitutes the ELCOMP output.

The ELCOMP output listing normally includes 400 to 1000 lines detected in the spectrum, their intensities, and 500 to 2000 associated chemical composition data. The approach used for interpreting this large quantity of data was to sort the assigned elemental composition into classes according to heteroatom composition (i.e., C,H; C,H,O; C,H,N; C,H,S) and degree of hydrogen unsaturation indicated by rings and double bonds. The R + DB value provides a convenient means of organizing data into probable chemical compound categories. Some examples will illustrate this point:

TABLE 10. REPLICATE EXTRACTIONS AND LC SEPARATIONS ON A SITE SOIL SAMPLE

	% Water	Dry Wt. Extracted (kg)	Extract TCO (mg)	Extract GRAV (mg)	Extract Total (mg)	Total (mg/kg)
Before LC Fractionation						
Sample 1: APN 0-6	15.9	0.0966	ND	9.0	9.0	93.2
Sample 2: APN 0-6	15.6	0.1090	ND	8.0	8.0	73.4
After LC Fractionation						
Sample 1: APN 0-6						
LC-H			0.82	1.67	2.49	25.8
LC-A			0.39	1.17	1.56	16.1
LC-X			ND	4.00	4.00	41.4
						83.3
Sample 2: APN 0-6						
LC-H			ND	1.17	1.17	10.7
LC-A			1.30	0.50	1.70	15.6
LC-X			ND	5.30	5.30	48.6
						74.9

for an n-paraffin, C_6H_{14}, R + DB = 0

for phenol, C_6H_6O, R + DB = 4

for benzothiophene, C_6H_6S, R + DB = 6

for anthracene, $C_{14}H_{10}$, R + DB = 10

for benzopyrene, $C_{20}H_{12}$, R + DB = 15

All paraffins or other saturated species such as acyclic alcohols and sulfides will always be in R + DB group 0. A species must have an R + DB value of 4 or more to be aromatic, and R + DB value of 7 or more to be a naphthalene, an R + DB value of 8 or more to be a polychlorinated biphenyl (PCB), and so on. The R + DB values were grouped in this report as follows: R + DB = 0, 1 R + DB 4; 5 R + DB 9; 10 R + DB 14; and 15 R + DB.

Similar calculations can be made for any species of interest. This approach does not differentiate among the different isomers of any compound class, such as anthracene and phenanthrene, in R + DB 10.

The R + DB and elemental composition values were then used to sort all of the data from HRMS analysis into a compact matrix first according to the R + DB value and second according to the elemental composition of each of the ions identified. This approach presents a simple view of the overall composition of a sample from a highly complex spectrum. This approach requires that all ions finally included in the matrix are parent (molecular) ions. However, a large number of fragment ions in the spectra complicates the analysis. In interpreting the HRMS data it is also necessary to account for isotope ions (e.g., ^{13}C and ^{37}Cl), and composition assignments with large experimental errors. Consequently, in developing the R + DB matrix, certain restrictions were applied in an attempt to eliminate interferences and questionable calculated compositions. The restrictions applied were:

Molecular Weight: Ions below 90 atomix mass units were excluded to minimize the interference from fragment ions.

Error: Calculated compositions which differed from measured values by more than 2 millimass units were excluded.

Isotopes: All calculated compositions that included isotopes such as ^{13}C, ^{34}S, and ^{37}Cl were excluded.

R + DB: Only compositions with integral R + DB values were included, thus excluding fractional R + DB values which arise from fragment ions.

Carbon No.: A minimum carbon number limit was set for each R + DB class.

For this report, the individual intensities of all ions within each R + DB and element group were summed to give a single estimate of the abundance of that group. For each composite sample, these estimates were subsequently displayed in a condensed form as shown in Figure 2.

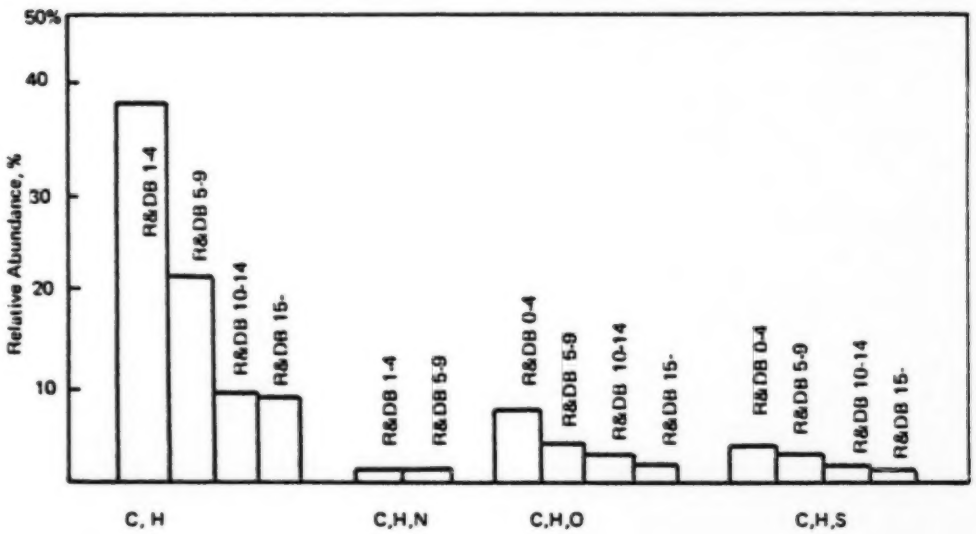

FIGURE 2 - EXAMPLE OF DISPLAY OF R+DB AND ELEMENTAL COMPOSITION GROUPINGS FOR A SOIL SAMPLE EXTRACT